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15 March 2000

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-2000-049**
Larson, C. William; Harper, Jessica; Presilla-Marquez, J.D. (Schafer Corp.), "Matrix Isolation of Boron
and Carbon Vapor. Control of Cluster Formation During Preparation and Annealing"

10th Internat'l IUPAC Conference on High Temperature Materials Chemistry (Statement A)
(Juelich, Germany, 10-14 April 2000) (Deadline: 31 March 2000)
(and Seminars at Max Planck Inst., Univ of Dortmund, Univ. of Basel, Apr 4, 7, 18

**Matrix Isolation of Boron and Carbon Vapor.
Control of Cluster Formation During Preparation and Annealing.**

J. D. Presilla-Márquez, J. Harper, C. W. Larson

Propulsion Directorate

Air Force Research Laboratory

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High Energy Density Matter (HEDM) Research Group

Pat Carrick (Chief), Jeff Sheehy (Group Leader), Greg Drake, Hi Young Yoo, Jeffrey Mills, Jerry Boatz, Jessica Harper,
Karl Christe, Mario Fajardo, Michael Tinnirello, Michelle DeRose, Paul Jones,
Txomin Presilla (Schafer Corporation) Peter Langhoff, Simon Tam, Suresh Suri, William Wilson,

**10th International IUPAC Conference on
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Forschungszentrum Jülich

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Universität Dortmund

Fachbereich Chemie

Anorganische Chemie

Dortmund, Germany

18 April 2000

**Kinetics of formation of cyclic C₆ and cyclic C₈ and of
B_JC_{n-J} clusters (J = 0, 1, 2; n = 3-11) in solid argon**

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Institute für Physikalische Chemie

Universität Basel
Basel, Switzerland
7 April 2000

**Kinetics of formation of cyclic C₆ and cyclic C₈ and of
B_JC_{n-J} clusters (J = 0, 1, 2; n = 3-11) in solid argon**

J. D. Presilla-Márquez, J. Harper, C. W. Larson

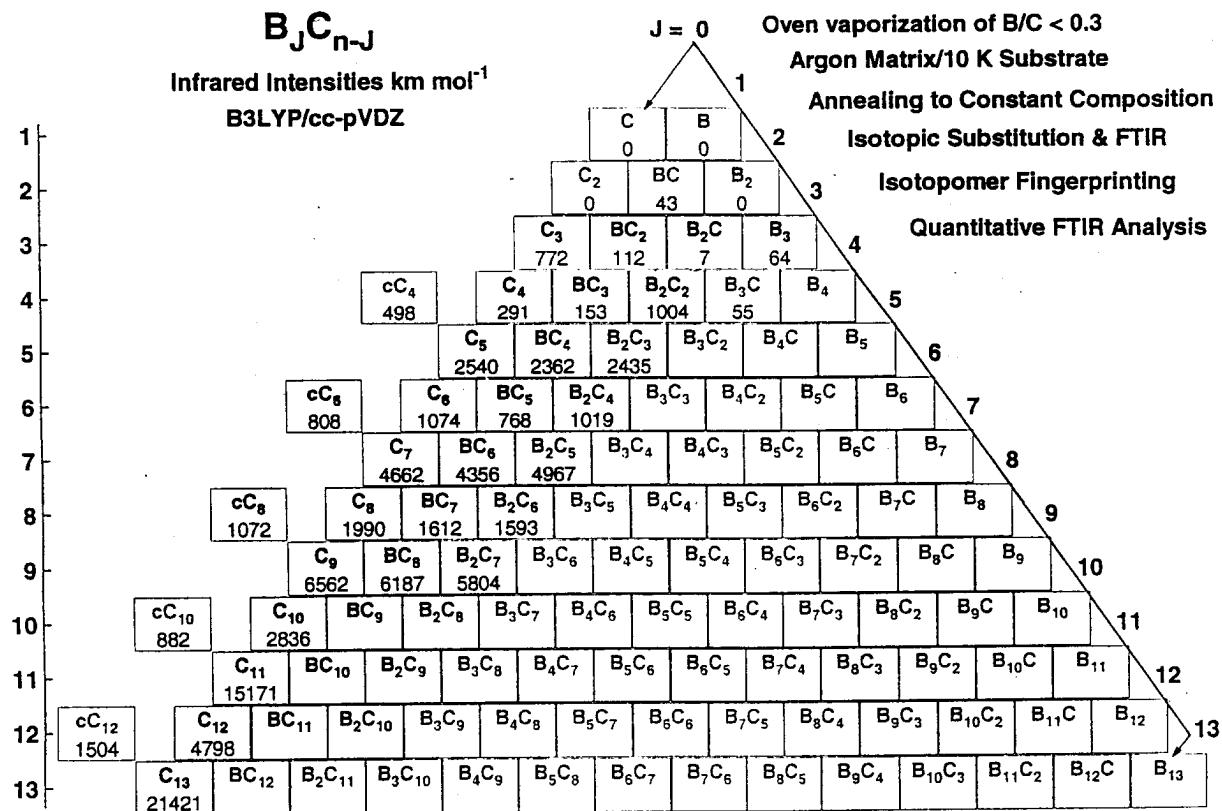
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**Max Planck Institute für Kernphysik
Heidelberg, Germany
5 April 2000**

GOAL - 5% atoms in matrix



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Goal

Production of cryogenic HEDM with five mole percent atoms.

Objective

Characterization of source and quantitative analysis of $B_J C_{n-J}$

Approach

Production of HEDM by evaporation of boron with high-temperature graphite furnace and co-deposition of vapor with argon on a cold (10 K) surface

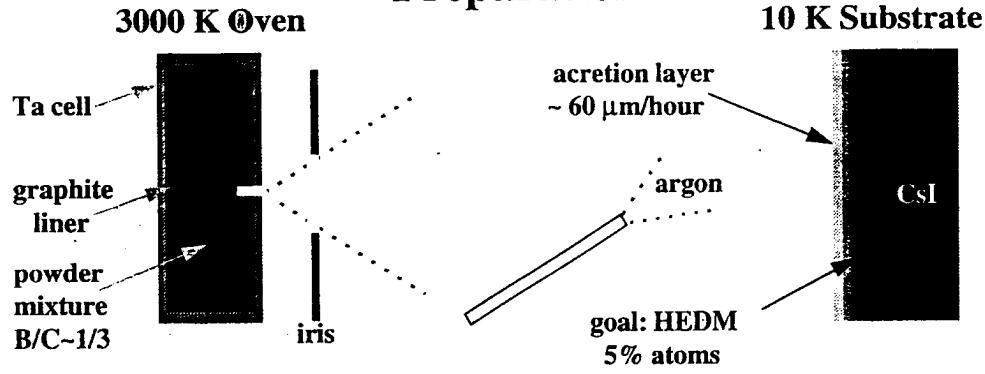
Identification and quantitative analysis of $B_J C_{n-J}$ species ($n \geq 3, J = 0$ to 2) by FTIR spectroscopy and *ab-initio* calculations.

Quantitative measurement of distributions of $B_J C_{n-J}$ species produced upon deposition and after annealing to a constant composition.

Determine absolute column densities (molecules cm^{-2}) from Beer's law:

$$\langle \rho_i \rangle = 2.303 A_{exp} / I_{theory}$$

Preparation

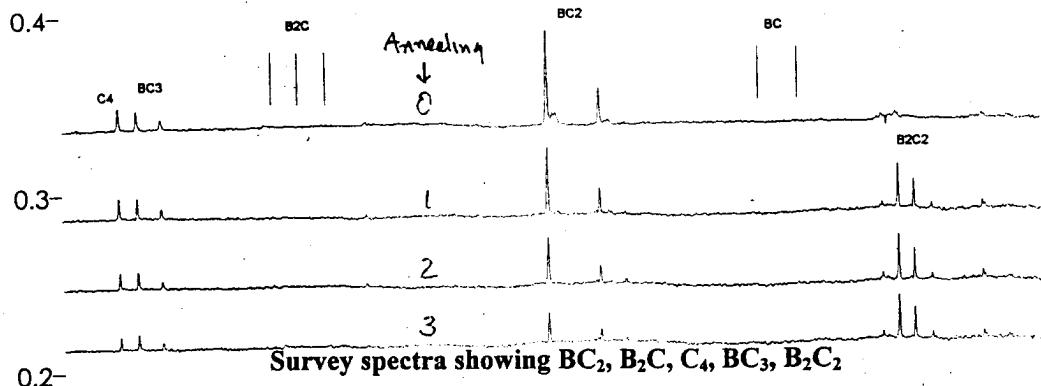


Annealing

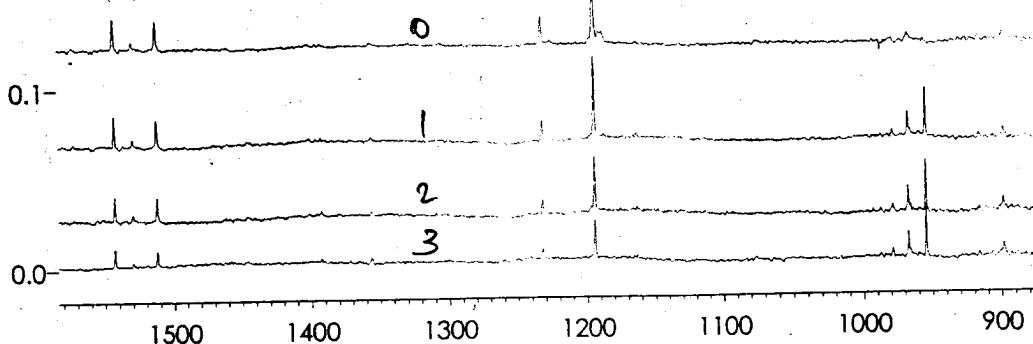
<u>a0</u> 10 K	<u>a3</u> 32.5 K, 60 s	<u>a6</u> 40.0 K, 20 s
<u>a1</u> 27.5 K, 120 s	<u>a4</u> 35.0 K, 45 s	sublimation
<u>a2</u> 30.0 K, 90 s	<u>a5</u> 37.5 K, 20 s	rate ~ 1 $\mu\text{m/s}$

Precision matched pair of matrices

Green Matrix $^{11}\text{B}/^{10}\text{B} = 80/20$ enhanced $^{11}\text{B}_j\text{C}_{n-j}$
Red Matrix $^{11}\text{B}/^{10}\text{B} = 27/73$ enhanced $^{10}\text{B}_j\text{C}_{n-j}$

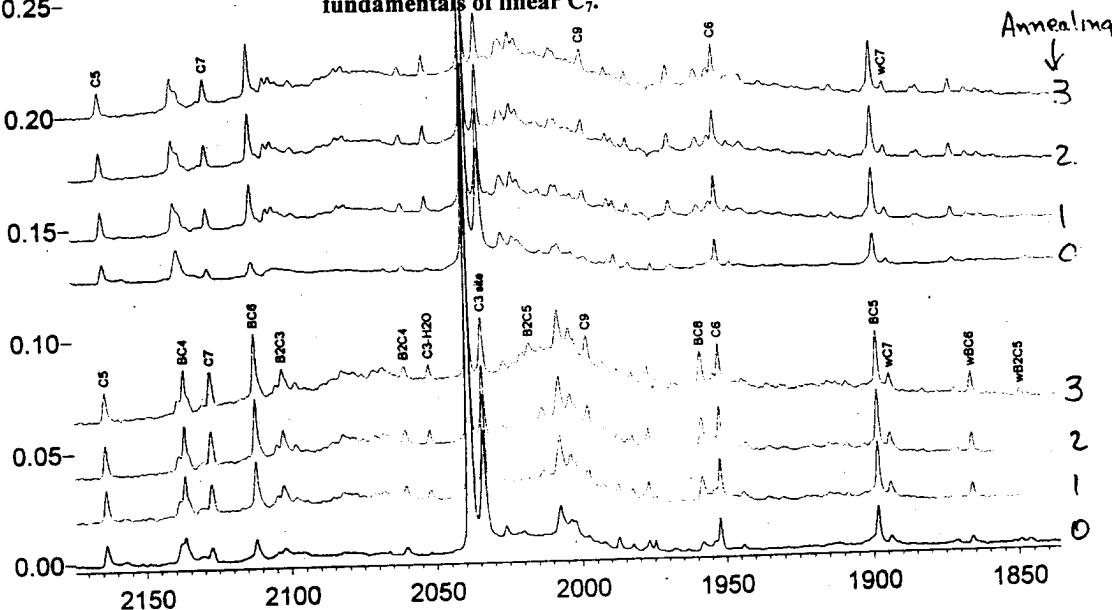


Doublet peaks belonging to ¹⁰BC_{n-1} and ¹¹BC_{n-1} and triplets belonging to ¹⁰B₂C_{n-2}, ^{10,11}B₂C_{n-2}, and ¹¹B₂C_{n-2} are seen with inverted intensity ratios. Note red shift of BC₃ from C₄. BC, B₃, and B₃C were not observed.

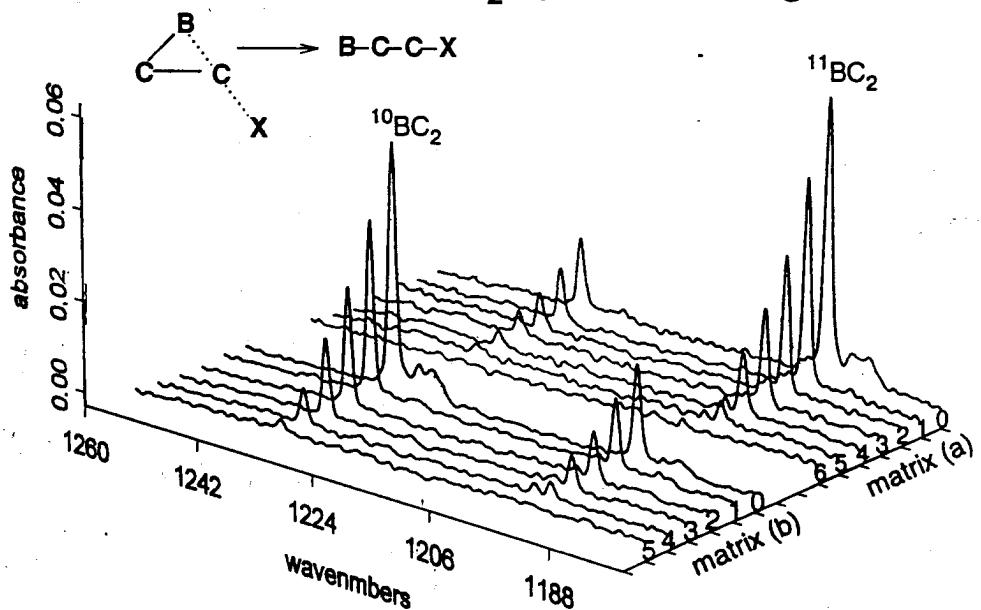


Survey spectra of precision matched matrices showing larger clusters
 $B_J C_{n-J}$, $n > 4$, $J = 0, 1, 2$ in original matrices and after three annealings.

Green (¹¹B/¹⁰B = 80/20) and Red (¹¹B/¹⁰B = 27/73) Matrices. All peaks except C₃ grow upon annealing. Fundamentals of BC_{n-1} for $n = 5, 6, 7$, and 9 are similarly red-shifted from fundamentals of linear C_n, and their experimental absorbances are all slightly greater. Two fundamentals of BC₆ are observed at 2112 and 1866 cm⁻¹, red-shifted from the two fundamentals of linear C₇.

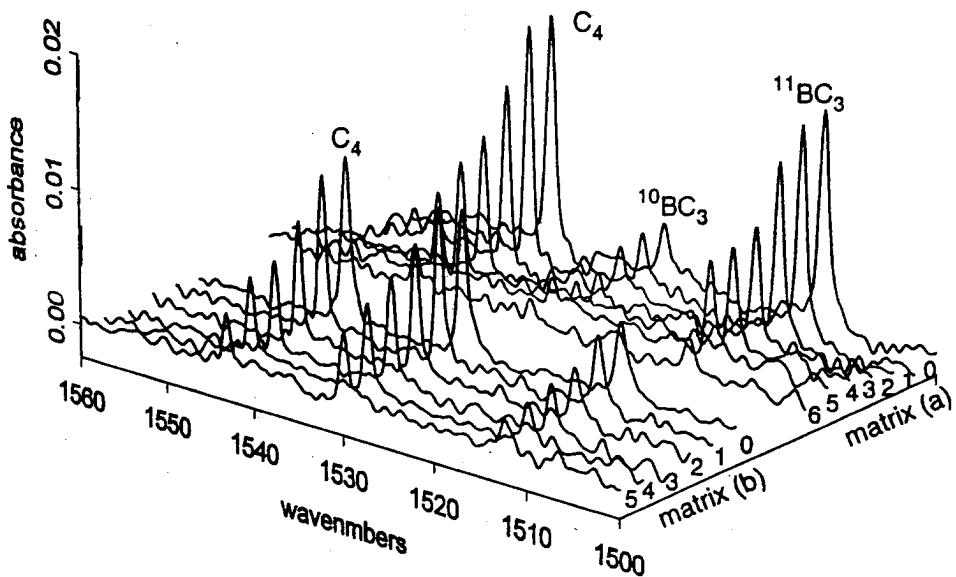
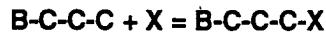


Disappearance of BC_2 upon annealing



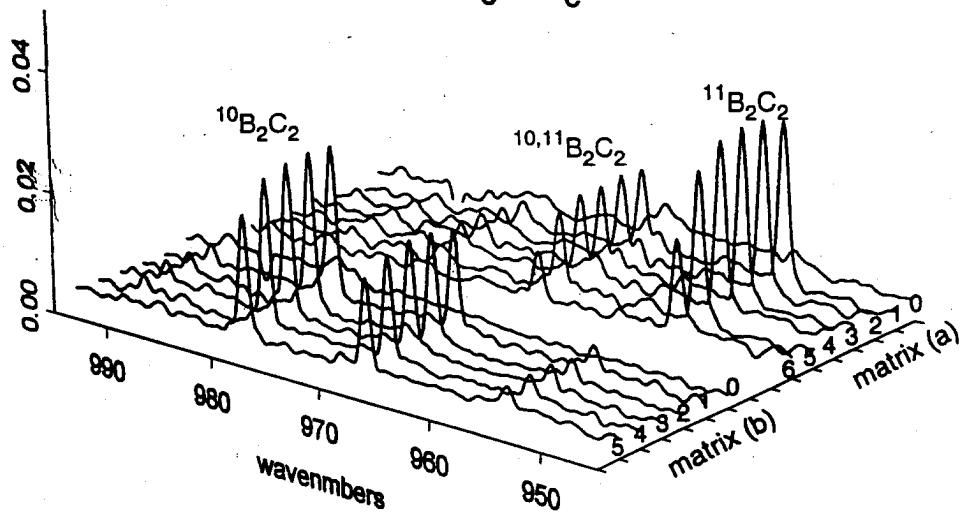
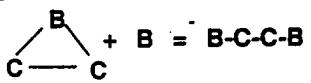
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Disappearance of BC_3 and C_4 upon annealing



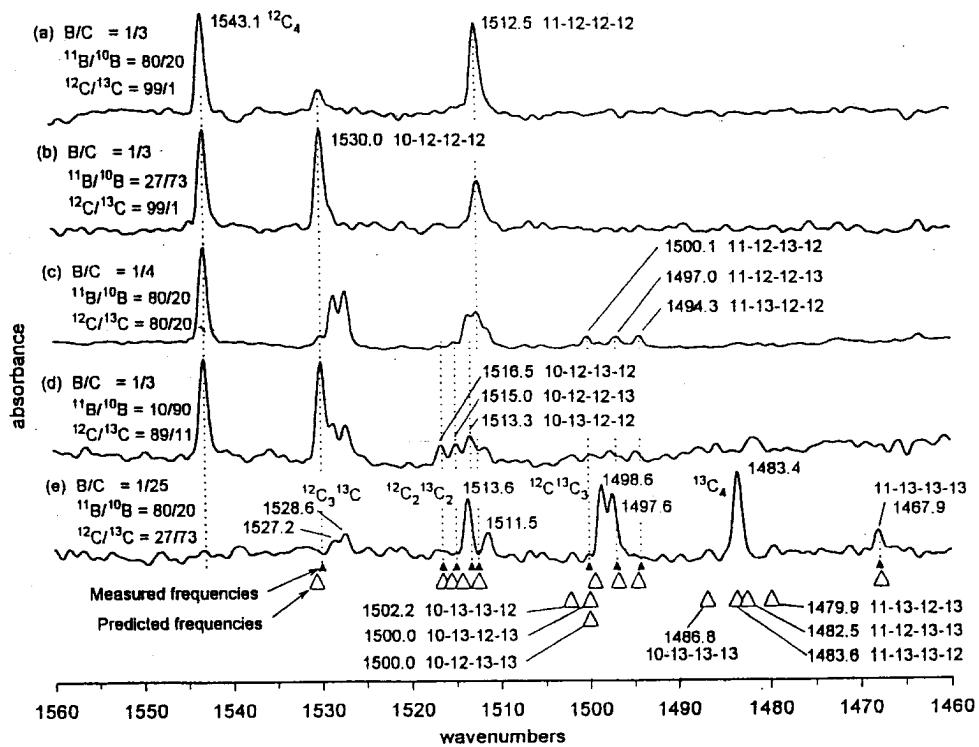
BC3rg3D2.axg Mar. 8, 2000 9:34:49 AM

Growth of B_2C_2 upon annealing

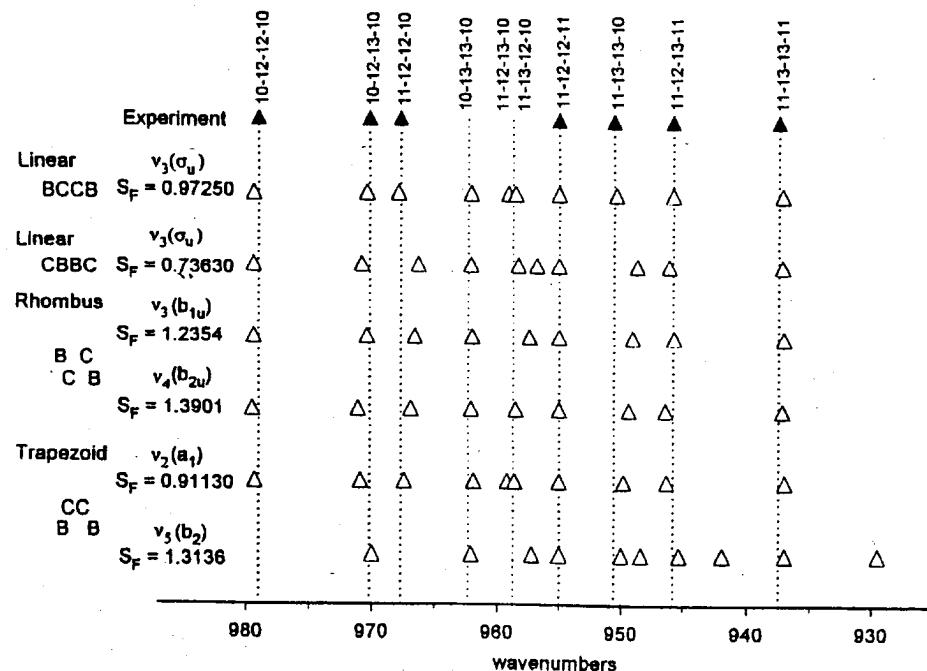


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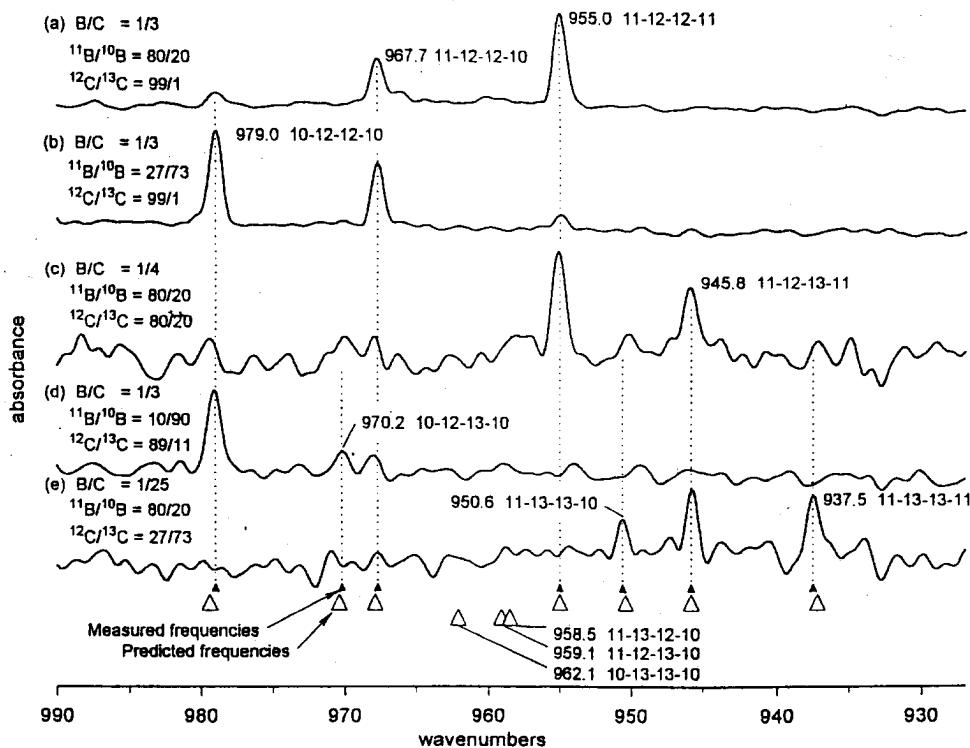
Identification of 9 of the 16 isotopomers of linear BCCC in 5 matrices.



Four minimum energy geometries of B_2C_2 produce similar isotopomer fingerprints.
 Scale factor (S_F = measured frequency/theoretical frequency) of linear BCCB = 0.97250.



Identification of 7 isotopomers of the 10 isotopomers of BCCB in 5 matrices.



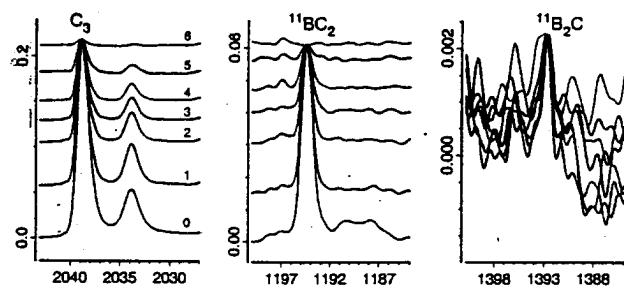
$B_J C_{n-J}$

Annealing Study

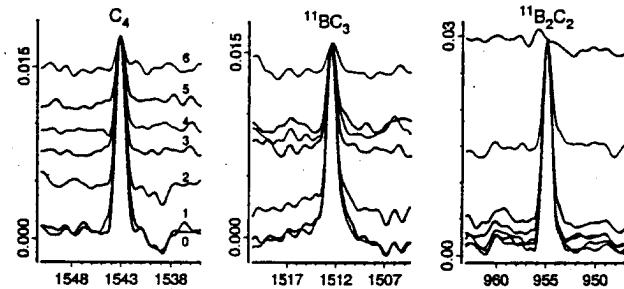
Peak by Peak

Detail

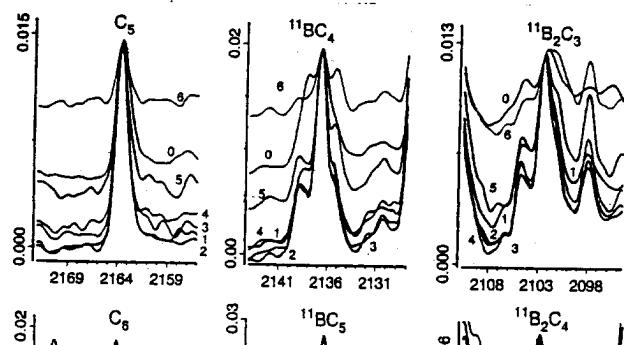
In first annealing C_4 and BC_3 remain constant and B_2C_2 grows from undetectable to S/N ~ 100 . B_2C_2 seems inert.



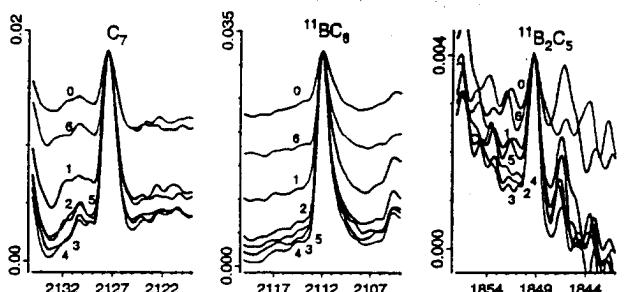
All pentamers grow in first annealing. B_2C_3 grows most; C_5 and BC_4 evaporate most in 5th annealing.



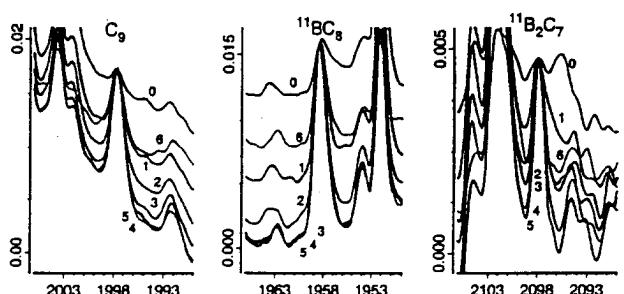
Hexamers with boron grow most; evaporation of C_6 in 6th annealing is greatest.



In 5th annealing, $J = 0$ evaporates more than $J = 1$, and $J = 1$ evaporates more than $J = 2$. A boron rich layer appears to be capped by a carbon rich layer.

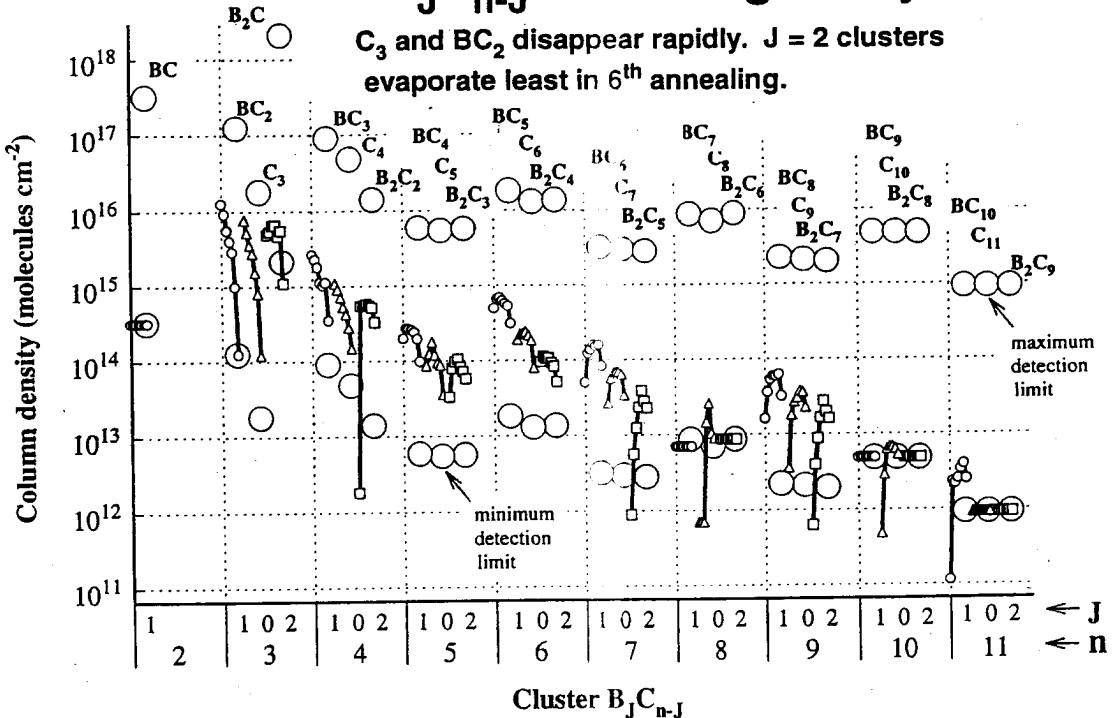


In 6th annealing, where almost half the matrix sublimed, the $J = 2$ clusters evaporate the least. A boron rich layer appears to be capped by a carbon rich layer.



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B_JC_{n-J} Annealing Study



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Results and Discussion

Linear C₃, cyclic BC₂, and cyclic B₂C, constituted about 80% of the total observable boron and carbon in the initially deposited matrix, but B₃ was not observed. If B₃ were present, its concentration fell below the detection limit of the system. The measured trimer distribution in the initially formed matrices was $\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1.5 : 0.5 : < 0.05$ (upper limit).

Statistical substitution of J boron atoms into an n -atom carbon cluster produces a distribution given by $\rho(B_J C_{n-J}) / \rho(C_n) = \{[n(n-1)\dots(n-J+1)]/J!\} [B/C]^J$. With the experimental B/C $\sim 1/3$, the statistical trimer distribution is

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1 : 0.33 : 0.03.$$

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

Linear C₃ and cyclic BC₂, disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B₂C was inert.

Linear C₄ and BC₃ (BCCC) disappeared more slowly, and linear B₂C₂ (BCCB) grew to $\sim 95\%$ of its final value during the first annealing. Once formed, B₂C₂, like B₂C, was also inert to further reaction.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2 .

The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2 .

Linear C_5 , BC_4 (BCCCC) and B_2C_3 (BCCCB) and larger linear clusters (B_JC_{n-J} , $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing.

The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$).

Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little ($< \sim 3$ kcal mol⁻¹) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature.

Conclusions

Annealing kinetics of disappearance of C_3 and BC_2 , and of appearance of B_2C , C_4 , BC_3 , B_2C_2 , C_5 , BC_4 , and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix.

~ 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers.

Molecules with two boron atoms are immune from radical attack and condensation during annealing.

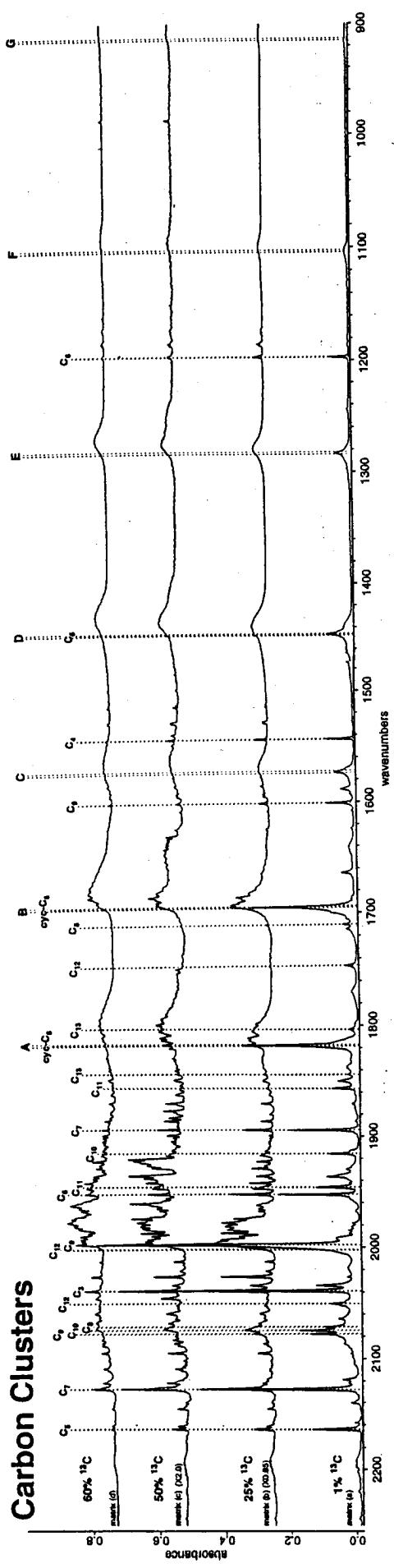
Future Work

Continued development of source for production of higher flux beam of nearly pure boron atoms.

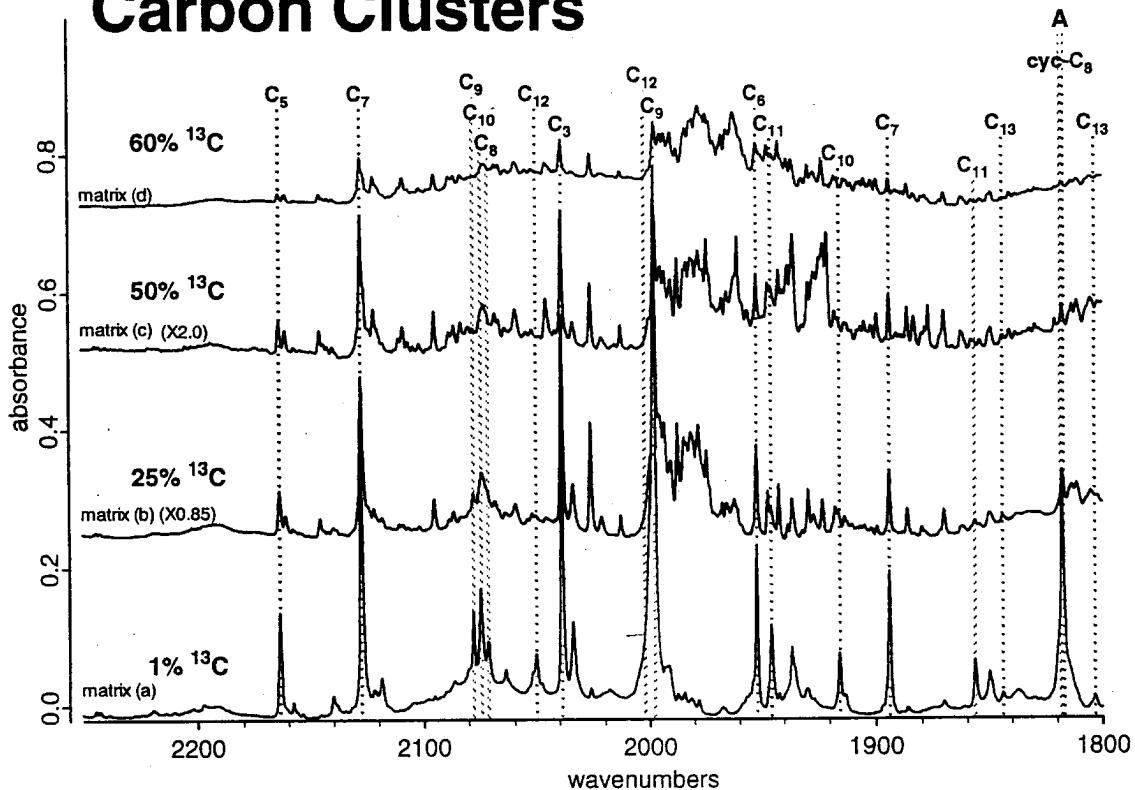
Map of "islands of stability" of pure boron HEDM; B_2 or B_3 may be the ultimate sink for atoms in the low temperature HEDM environment.

Determine reactivity of boron atoms with hydrogen during co-deposition.

Develop rapid condensation methodology to prevent reaction of B with H_2 .

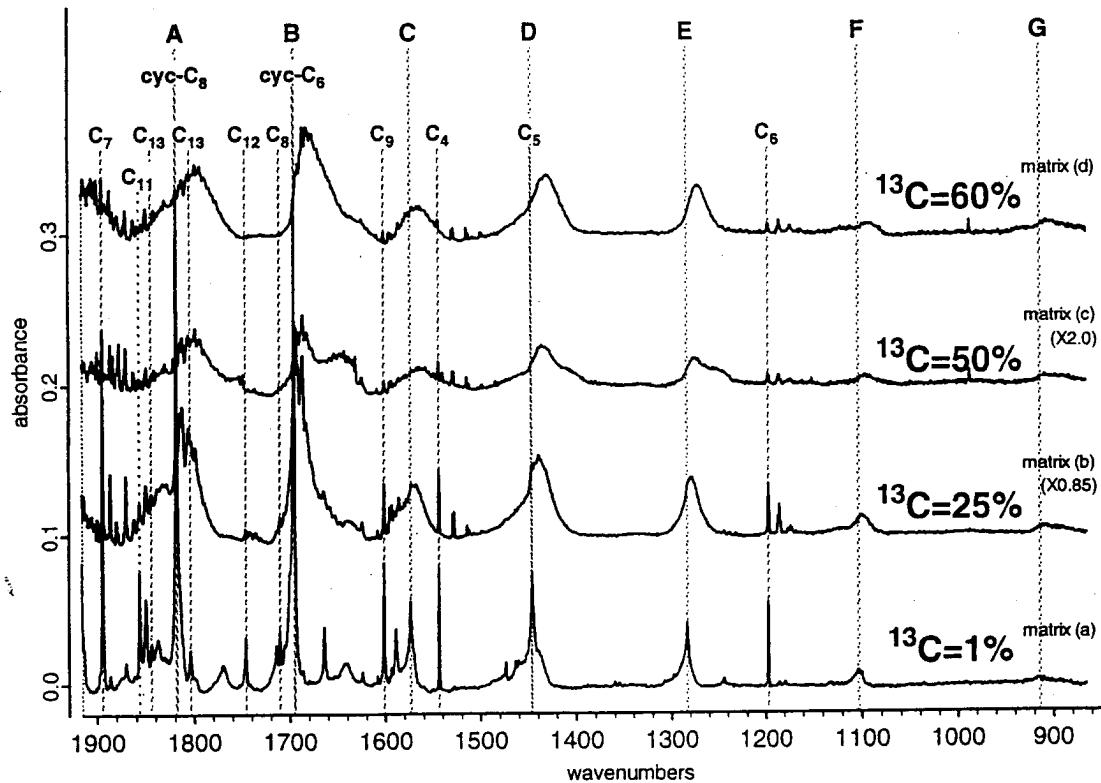


Carbon Clusters



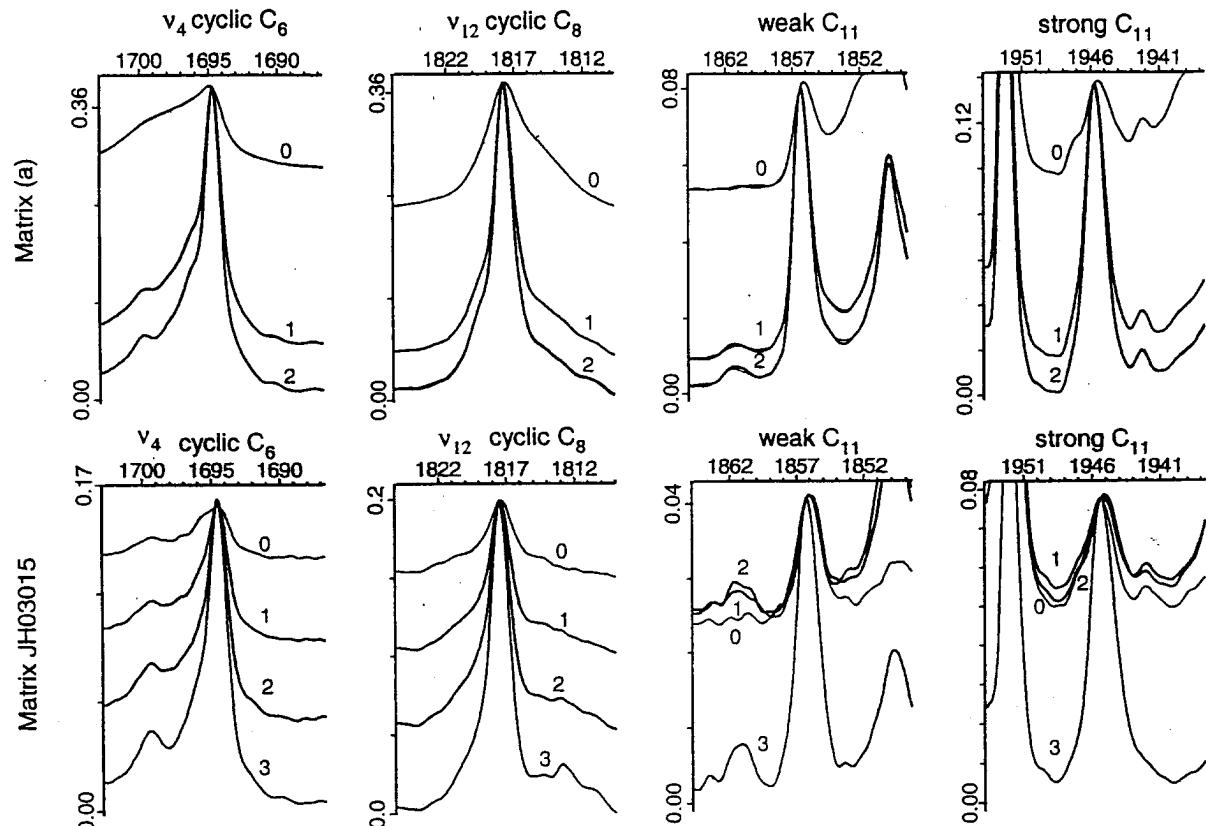
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Carbon Clusters



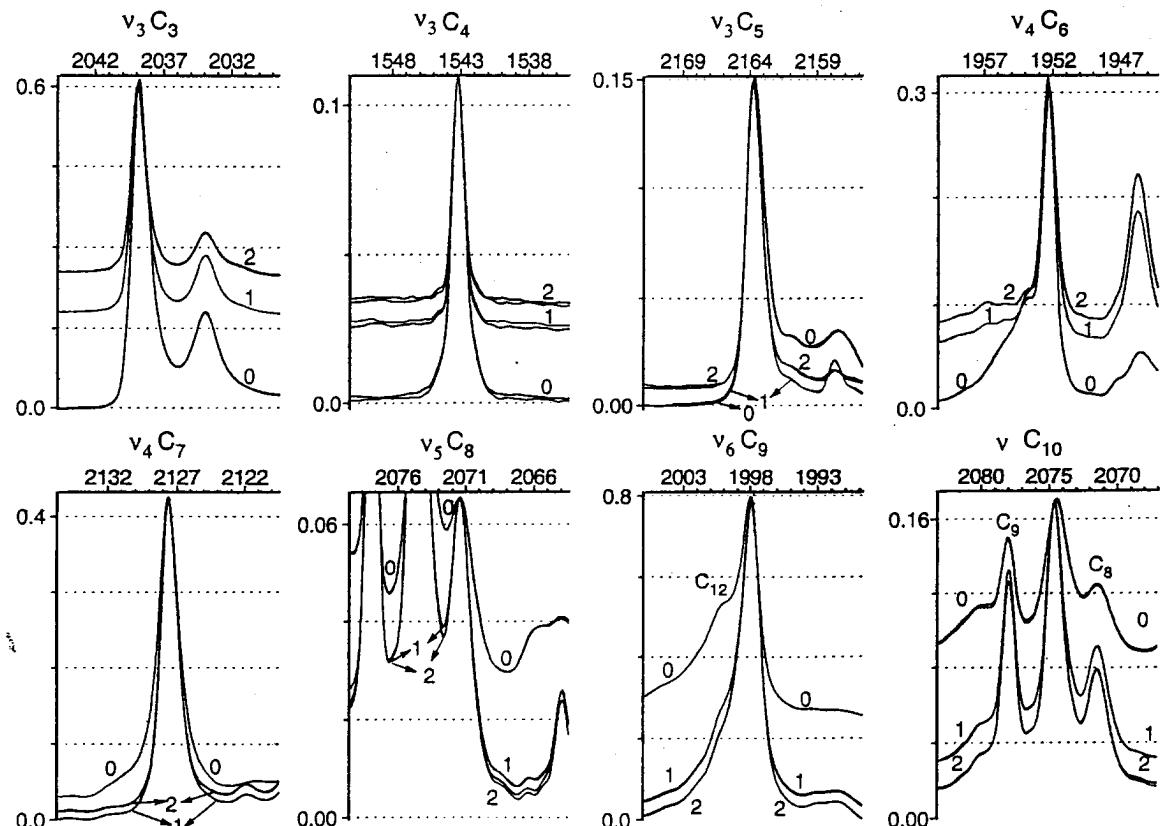
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Growth upon annealing - cC_6 and cC_8 - two fundamentals of C_{11}

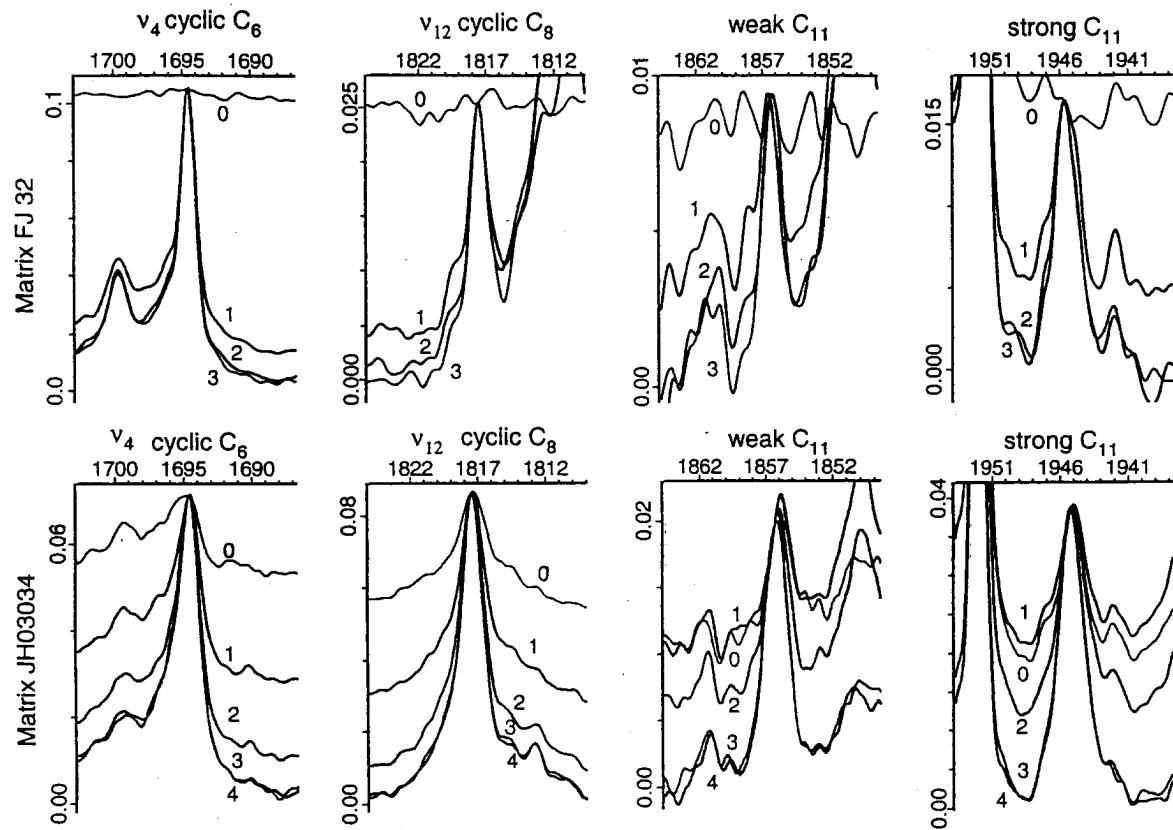


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Carbon Matrix (a) - Linear C_3 to C_{10} Clusters



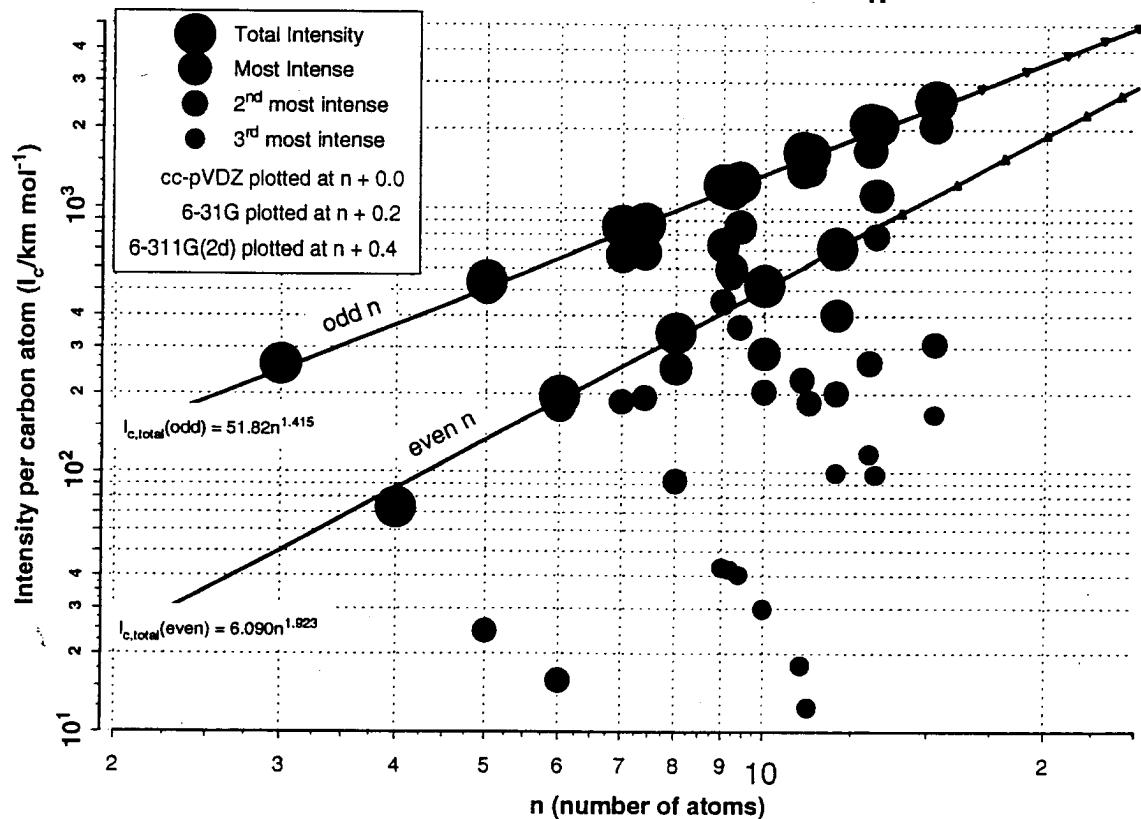
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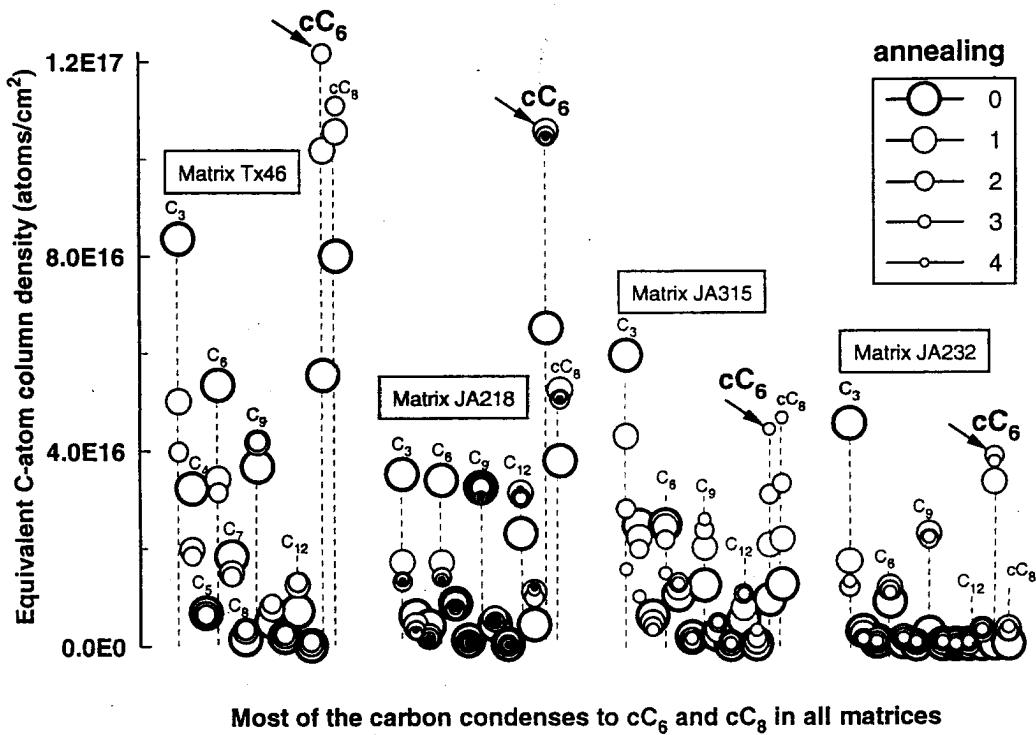
Carbon Matrix FJ 32, JA03034

MaCCn5.axg July 8, 1999 7:56:39 AM

Theoretical Infrared Intensities of Linear C_n , DFT/B3LYP



Carbon cluster distributions



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Conclusions from Carbon HEDM Research

Quantitative analysis - Establishes HEDM density, distribution of carbon clusters, tracking of growth and decay of carbon clusters, carbon bookkeeping - quantification of "invisible carbon", C-atom and C₂.

Highest density matrix (equivalent C-atom density ~ 1 mole percent in argon) contained 40% "invisible" carbon (C, C₂), determined by tracking the growth of the "visible" (measurable) carbon to a constant composition after repeated annealing. Main product of condensation is cyclic C₆.

Yields of cyclic-C₆ are a factor of two larger than the combined yield of all other clusters in the fully condensed, highest density matrices. Cyclic-C₆ is the dominant condensation product.

Substrate must be shielded from oven to prevent condensation during deposition. Higher temperature oven places higher heat load on substrate, which promotes condensation.

Obtained higher density matrices by decreasing argon flux and maintaining oven flux. However, condensation was also increased.

Matrices produced with argon/5% H₂ caused nearly complete loss of C_{n+1} and C_{n+2} relative to C_{n+3}, suggesting that H₂ scavenges C-atoms efficiently during co-deposition.